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SYNTHESIS OF POLYHETERODARYLENES FOR HIGHLY
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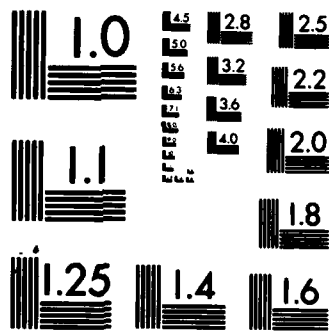
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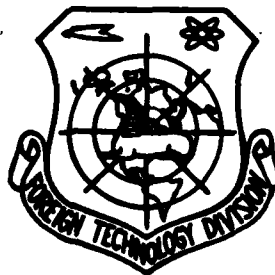
FOREIGN TECHNOLOGY DIVISION



SYNTHESIS OF POLYHETEROARYLENES FOR HIGHLY
HEAT-RESISTANT MATERIALS

by

A. Ya. Chernikhov, L. A. Rodivilova, et al



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FTD-ID(RS)T-0351-84

4 April 1984

MICROFICHE NR: FTD-84-C-000347

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English pages: 7

Source: Plasticheskiye Massy, Nr. 4, April 1973, pp. 24-27

Country of origin: USSR

Translated by: Victor Mesenzeff

Requester: FTD/TQTR

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after ь, ы; e elsewhere.
When written as ë in Russian, transliterate as yë or ë.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh ⁻¹
cos	cos	ch	cosh	arc ch	cosh ⁻¹
tg	tan	th	tanh	arc th	tanh ⁻¹
ctg	cot	cth	coth	arc cth	coth ⁻¹
sec	sec	sch	sech	arc sch	sech ⁻¹
cosec	csc	csch	csch	arc csch	csch ⁻¹

Russian English

rot curl
lg log

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SYNTHESIS OF POLYHETEROARYLENES FOR HIGHLY HEAT-RESISTANT MATERIALS

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G. V. Bogachev.

Among the various synthetic highly heat-resistant polymers, at the forefront is a large class of compounds which are grouped under the common name of polyheteroarylenes. Aromatic polymers with heterocycles in the chain have different properties, which determines their broad application in the future.

However, despite the sufficiently comprehensive data on the ways to obtain polyheteroarylenes and on the properties of the synthesized polymers, an overwhelming majority of these highly heat-resistant polymers has not found practical application as of yet. This is connected with a number of objective reasons, one of which is the difficulty of processing of the most heat-resistant polymers. We are still faced with a very difficult problem of obtaining polyheteroarylenes with a large molecular weight, without defects in the structure of the polymer chain (including 100% of ring formation), with total absence of side products and impurities which cause the formation of micropores and microdefects in the articles, having the capacity of retaining high physicomechanical indices over a long period of time at temperatures above 300°C, and which are easily processed.

It is a known fact that the polycondensation technique, which is accomplished in one or two stages, is the most popular method of synthesizing polyheteroarylenes. The principal advantage of the single-

stage method is a high degree of completion of the polymer structure. Since the formation of the polymer chain occurs, in this case, simultaneously with the formation of heterocycles, such a method makes it possible to obtain completely cyclized polymers. The process takes place in a medium possessing the properties of a strongly condensing agent. Thus, many polyheteroarylenes of large molecular weight were obtained in polyphosphoric acid. However, this method also has significant drawbacks. First of all, this pertains to the difficulty of complete processing of aromatic polyheteroarylenes, which is due to their affinity for associative interactions, which are characteristic for all polyconjugated systems [1]. The intermolecular forces in these polymers can be so great, while molecular mobility so low, that they do not dissolve in none of the known solvents and do not soften right up to the temperature at which decomposition begins.

The only possible way in which such polymers can be used in materials is the so-called high-temperature sintering, which makes it possible to obtain monolithic samples resulting from holding the polymer powder under pressure at temperatures, which are close to that at which decomposition begins.

Taking into account that the associative interactions, which determine the difficulties in processing, depend substantially on the system of polyconjugation and the packing density of macromolecules, a proposal was made to modify the polymer chains with bulk substituents. The presence of such fragments in the chain leads to the disruption of the polyconjugation system and formation of a looser structure during packing of the macromolecules in the solid phase. On the whole, this has a bearing on the molecular mobility of the polymer and is manifested in the form of ability to dissolve in polar solvents and to soften at higher temperatures. It is necessary to note that the thermal stability of the polymer is also reduced at the same time.

The two-stage method of obtaining polyheteroarylenes is also of interest. In this case, the processing of a polymer, for example, in the form of solutions can now be accomplished after the first stage, when polymer chains with an intermediate structure have been formed, while the most rigid and thermostable structure is formed during the second stage. For this, that or another reaction of intermolecular cyclization is often used.

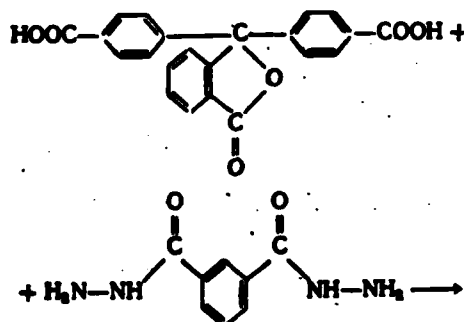
A significant drawback of the two-stage method is, first of all, the impossibility of attaining 100% of macromolecular transformation. No matter how thoroughly the cyclization conditions are selected for a pre-polymer, the end product will always be characterized by a certain degree of incompleteness of the aromatic structure, by a defect of one type or another.

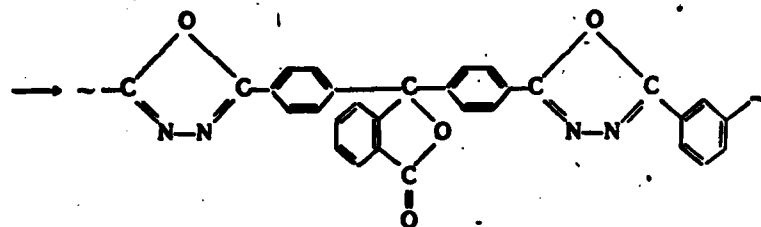
Moreover, most of the known cases are associated with the formation of considerable amounts of low-molecular products - of the type of water or ammonia - during the cyclization stage. In this case, it is necessary to take into account that cyclization of a pre-polymer takes place at temperatures up to 250-350°C and, even in the case of thin films (5-10 μ), the "hot" molecules of the low-molecular products, on their way out of the material, have to traverse a path which is tens of thousands greater than the intermolecular distances. Consequently, the low-molecular products produced during cyclization can be the reason for the destructive processes - formation of micropores and micro-defects in the material.

Thus, each of the methods mentioned above for obtaining heat-resistant polyheteroarylenes has both positive and negative sides.

In order to select the most promising direction in the area of creating highly heat-resistant materials based on polyheteroarylenes, we investigated the processes of obtaining poly-1, 3, 4-oxadiazoles (POD) and polybezoxazoles (PBO).

It was decided to use the one-stage method for obtaining poly-1, 3, 4-oxadiazoles with the use of polyphosphoric acid as the medium and the condensing agent. The experiments have shown that the best results are obtained from a cyclopolycondensation reaction between 4,4'-diphenylphthalidedicarboxylic acid and dihydrazide of isophthalic acid [2]:

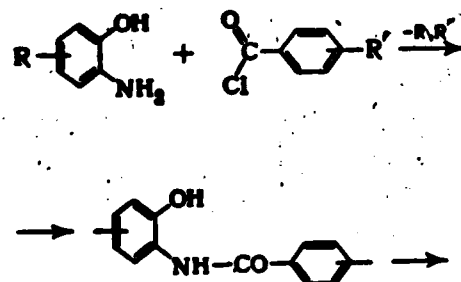




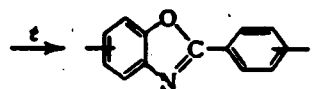
The polymer product that was obtained was called POD-2. In analyzing the synthesis, certain difficulties were associated with the absence of data on the use of polyphosphoric acid on the experimental or experimental-industrial scales for obtaining polyheteroarylenes. It is necessary to note that polyphosphoric acid has a significant viscosity even at elevated temperatures. This has a strong effect on the kinetics of the reaction and complicates the procedure of controlling the process. Thus, a problem was formulated which involved analyzing each individual stage in succession - from preparation of the polyphosphoric acid to obtaining and refinement of the final poly-1, 3, 4-oxadiazole.

The test conducted on the polymer as a binder for laminated plastics have confirmed the correctness of the synthesis conditions selected. Thus, fiber glass plastics based on the fabric TS-8/3-2500 and polymer POD-2 retained their ultimate strength during bending ($\sigma_{\text{B}}^{300^\circ\text{C}}$) at the level of 1500 kg/cm^2 after being kept for several hundred hours at 300°C . At the present time, the studies of this process are aimed at finding additional ways in which stable indices at higher temperatures can be obtained.

Another polymer, which was obtained in the experiments, is oxolone, which is in the class of polybenzoxazoles. The most thermostable structure of oxolone is formed not in one stage, as that in POD-2, but in two stages. As a result of low-temperature polycondensation, polyoxamide



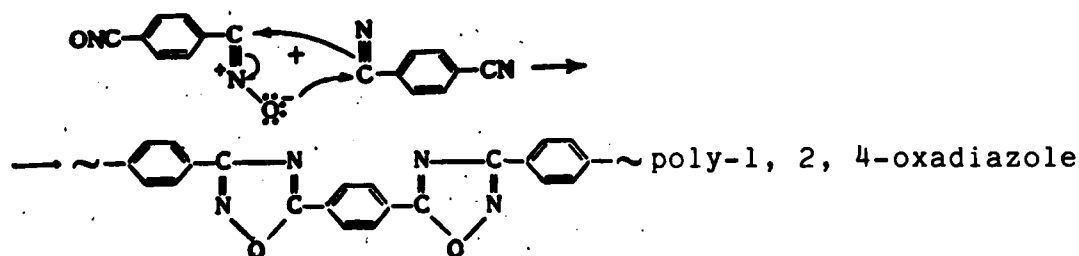
is formed in bis-o-aminophenol with dichloroanhydride of dicarbonic acid during the first stage, which transforms into polybenzoxazole



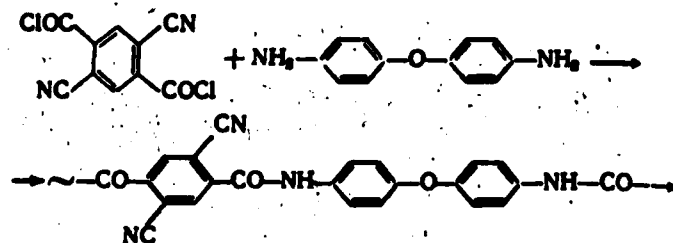
during the second stage as a result of heat treatment under vacuum or in an inert medium at 280–320°C.

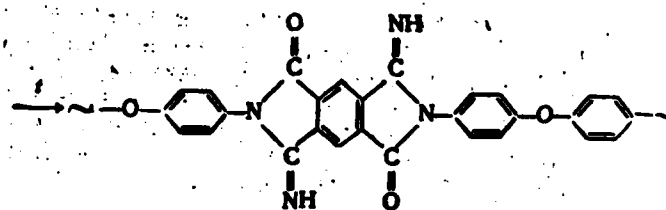
Subsequent processing of polybenzoxazole in air leads to cross-linking of polymer chains which, according to the IR spectroscopic studies, proceeds with the participation of the methylene groups. The preliminary tests conducted on oxolone as a binder for fiber glass plastics have shown that it can be used for structural materials which operate long periods of time at 300°C.

One of the new directions of these studies is associated with the creation of polymers based on monomers containing nitrile groups. This is particularly important in view of the fact that a nitrile group can take part in the formation of strong heterocycles, which proceeds without the formation of low-molecular by-products. We can give the following 1, 3-dipolar polyaddition reaction between terephthalonitrile and terephthalonitrile N-oxide as an example [3]:



The unions with the nitrile groups can also be used for two-stage processes. Thus, dichloroanhydride of dicyantereophthalic acid and diaminodiphenyl esters were used to obtain polycyanamide





which transforms to polyiminomide at 250–350°C [4]. Based on the preliminary data, polymers so structured can be a base for the materials intended for use at 350°C for long periods of time. On the whole, the prospects for creating high-strength and highly thermostable materials based on polyheteroarylenes are connected with the development of new methods for processing highly heat-resistant, rigid-chain polymers (for example, high-temperature pressure sintering) and also with finding ways of obtaining the most stable structures during the process or after the articles have been formed.

The first approach should be connected, to considerable extent, with reprocessing of the known polymers and requires the undertaking, along with comprehensive physicochemical studies, of a serious engineering and technological critical analysis of the processes realized at temperatures up to 400–500°C and pressures up to several thousand atmospheres.

The second approach is, to a greater extent, synthetic. In this case, it can be assumed that at the top of the list is a study that should be conducted on the different variants of polycyclization without the formation of by-products, as this happens, for example, in polycyanamides. It is also possible to expect a certain amount of success from the studies of the dipolar polyaddition reactions [5], which also make it possible to synthesize thermostable heterocyclic polymers without the formation of any by-products. In this regard, oligomer products with the corresponding reactive groups are of particular interest.

As was shown by the experiments that were conducted, certain possibilities still advocate the addition of bulk fragments to the composition of polymer chains. Thus, poly-1, 3, 4-oxadiazoles based on triptycene derivatives possess extremely high solubility even though the rigidity of polymer chains, according to rheological tests, in these polymers is higher than in the analogous poly-1, 3, 4-oxadiazoles based on 4,4'-diphenylphthalidedicarbonic acid. The stabilization of heat-resistant polymers of the polyheteroarylenes type has not been studied at all. The positive results of the preliminary tests make it possible

to hope that the service life of such polymers as POD-2 and oxolone can be increased.

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